"WHAT IS THE EFFECT OF ADDITION OF POTASSIUM, SODIUM AND BARIUM NITRATES ON THE EMULSIFYING ACTION OF SURFACTANTS SODIUM PALMATE AND SODIUM LAURYL **ETHER SULPHATE?**"

A common problem faced by households with hard water when using soap is lime soaps or soap scum. Calcium or magnesium in hard water replace sodium and react with fatty acid component of soap, forming insoluble scum.<sup>23</sup>



Figure 6: Soap micelle with carboxylate head groups of soap interacting with counter-ions and water<sup>24</sup> 2.3 Detergent

Detergent is another wa combines with impurities suractan differs from soap in not forming a scum mem mo D with salts in hard water.<sup>25</sup> Detergents contain alkylbenzenesulfonates, a family of compound that is similar to soap.<sup>26</sup>

An example of detergent is sodium lauryl ether sulphate (SLES), structural formula shown below.

<sup>25</sup> Oxford Dictionaries. Detergent. http://oxforddictionaries.com/definition/english/detergent (Accessed February 14, 2013)

<sup>&</sup>lt;sup>23</sup> Helmenstine. About.com Chemistry, How Soaps Cleans.

http://chemistry.about.com/od/cleanerchemistry/a/how-soap-cleans.htm (Accessed February 14, 2013)

<sup>&</sup>lt;sup>24</sup> New Mexico State University. Solubility.

http://web.nmsu.edu/~snsm/classes/chem116/notes/solutions.html (Accessed January 5, 2013)

<sup>&</sup>lt;sup>26</sup> Salager, Jean-Louis. Surfactants Types and Uses. http://www.nanoparticles.org/pdf/Salager-E300A.pdf (Accessed February 14, 2013)

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An EDL consists of three parts: 1) Surface charge - charged ions adsorbed on the micelle surface. 2) Stern layer – counter-ions (charged opposite to the surface charge) attracted to the micelle surface and closely attached to it by electrostatic force. 3) Gouy-Chapman Layer or diffuse layer: a film of the dispersion medium (solvent) adjacent to the micelle. Gouy-Chapman layer comprises free ions with a higher concentration of the counter-ions.<sup>40</sup> The ions of Gouy-Chapman layer are affected by the electrostatic force of the charged micelle.



Figure 11: Electric double layer of a negatively charged particle<sup>41</sup>

Cation has the effect of compressing the Gouy-Chapman layer of anionic micelles decreasing the thickness of this layer. The extent of compression is dependent on the valence of the cation.<sup>42</sup> For example, barium ions have two valence compared to sodium ions. Thus, barium ions would be expected to compress the Gouy-Chapman layer of the micelle more than sodium ions.

http://www.substech.com/dokuwiki/doku.php?id=surfactants (Accessed January 5, 2013)

<sup>&</sup>lt;sup>40</sup> Dmitri Kopeliovich, Substances & Technologies. Surfactant.

<sup>&</sup>lt;sup>41</sup> Ceramic Industry. Measuring Zeta Potential. http://www.ceramicindustry.com/articles/measuringzeta-potential (Accessed May 23, 2013)

<sup>&</sup>lt;sup>42</sup> Paton-Morales, P.; Talens-Alesson, F.I. Effect of Competitive Adsorption of Zn<sup>2+</sup> on the Flocculation of Lauryl Sulfate Micelles by Al<sup>3+</sup>. *Langmuir* [Online] **2002**, *18*, 8295-9301

http://homepage.ntlworld.com/federico.talens-alesson/plagio/la0200820.pdf (Accessed March 23, 2013)



Figure 28: Soap solution with NaNO<sub>3</sub> being heated and stirred for 10minutes





Figure 30: Detergent solution with NaNO<sub>3</sub> being heated and stirred for 10minutes

8. Stir the mixtures again with the magnetic stirrer at stirring scale of 7 and heating scale of 3 for 20 minutes timed with a digital stopwatch.



Figure 34: Soap solution with NaNO<sub>3</sub> being heated and stirred for 20minutes



Figure 35: Detergent solution with NaNO3 being heated and stirred for 20minutes

#### 4.3.1 Detergent

	1	2	3
Initial Vol of	0.00	12.20	23.20
HNO <sub>3</sub> / cm <sup>3</sup>			
±0.05cm <sup>3</sup>			
Final Vol of	12.20	23.20	34.20
HNO <sub>3</sub> / cm <sup>3</sup>			
±0.05cm <sup>3</sup>			
Vol of HNO <sub>3</sub>	12.20	11.00	11.00
used / cm <sup>3</sup>			
±0.10cm <sup>3</sup>			
Readings taken		$\checkmark$	$\checkmark$

## Table 4.3.1.1: Detergent solution

## 4.3.2 Detergent - NaNO<sub>3</sub>

	Table 4.3.2	.1: Detergent solut	tion containing Nat	to.uk
		1	4620	3
	Initial Vol of	0.00	13.00	25.10
	HNO <sub>3</sub> / cm <sup>3</sup>	rolli	A 94	
	±0.05cm <sup>3</sup>			
	Final (Close	13.00	25.10	37.30
P	HNO <sub>3</sub> / cm <sup>3</sup>	pag		
	±0.05cm <sup>3</sup>			
	Vol of HNO <sub>3</sub>	13.00	12.10	12.20
	used / cm <sup>3</sup>			
	±0.10cm <sup>3</sup>			
	Readings taken			

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# 4.3.3 Detergent - KNO<sub>3</sub>

	1	2	3
Initial Vol of	0.00	13.30	25.60
HNO <sub>3</sub> / cm <sup>3</sup>			
±0.05cm <sup>3</sup>			
Final Vol of	13.30	25.60	38.00
HNO <sub>3</sub> / cm <sup>3</sup>			
±0.05cm <sup>3</sup>			
Vol of HNO <sub>3</sub>	13.30	12.30	12.40
used / cm <sup>3</sup>			
±0.10cm <sup>3</sup>			
Readings taken			

### Table 4.3.3.1: Detergent solution containing KNO3

## 4.3.4 Detergent - Ba(NO<sub>3</sub>)<sub>2</sub>

	Table 4.3.4.1	: Detergent solution	on containing Ba(N	eo.uk
		1	462°	3
	Initial Vol of	0.00	15.70	30.70
	HNO <sub>3</sub> / cm <sup>3</sup>	rolli	A 94	
	±0.05cm <sup>3</sup>		01 -	
	Final (Close	15.70	30.70	45.70
P	HNO <sub>3</sub> / cm <sup>3</sup>	pag		
	±0.05cm <sup>3</sup>			
	Vol of HNO <sub>3</sub>	15.70	15.00	15.00
	used / cm <sup>3</sup>			
	±0.10cm <sup>3</sup>			
	Readings taken			

## 5. DATA PROCESSING

## 5.1 Sample Calculation

Only a sample calculation is shown here. All calculations can be found in Appendix C. The general formulas for the calculations can be found in Appendix D.

## 5.1.1 Control Set

NaOH reacted:



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and Bases (HSAB). HSAB states that hard ligands favour bonding to hard cations, soft ligands correspondingly favour bonding to soft cations. According to the Lewis definition of acid and bases, ligands which are electron donors are bases, while cations which are electron acceptors are acids. The hardness of acid and base is dependent on size and ease of polarizing. The smaller and non-polarizable the acid and base, the harder it is. Hence, hardness of the hexa-aqua univalent ion acids utilized is ordered as  $[Na(H2O)_6]^+>[K(H2O)_6]^+$ , with sodium possessing a more extensive hydration shell.



Figure 45: Thermodynamics of hydrophobic interactions<sup>60</sup>

This is evidenced by more exothermic  $\Delta H^{\Theta}_{hyd}$  of Na<sup>+</sup> of -416kJmol<sup>-1</sup> compared to -322kJmol<sup>-1</sup> of K<sup>+</sup>. Na<sup>+</sup> is readily hydrated and favours interaction with the

<sup>&</sup>lt;sup>60</sup> ChemWiki: The Dynamic Chemistry Textbook. Hydrophobic interactions.

http://chemwiki.ucdavis.edu/Physical\_Chemistry/Physical\_Properties\_of\_Matter/Intermolecular\_For ces/Hydrophobic\_interactions (Accessed April 2, 2013)



Figure 48: Shape transitions of micelle due to increased ionic strength68

## 6.6 Gibbs free energy

With reference to results obtained, electrostatic energy and binding heat are less endothermic and more exothermic for Ba<sup>2+</sup> compared to the univalent ions implying that overall enthalpy of micellization for Ba<sup>2+</sup> is more exothermic. For the comparison between sodium and potassium, differences in binding heat and extensiveness of hydration shell between these ions account for slightly better oil emulsifying ability of potassium ions related to sodium.

A reaction is only feasible if the Gibbs has energy, which can be derived from the formula  $G = \Delta H$ . The energy G is Gibbs free energy,  $\Delta H$  is enthalpy change, T is there entry and  $\Delta S(c)$  change in entropy, is negative. Hence, a decrease in  $\Delta H$  (more exothermic) causes a decrease in G. Therefore, formation of micelles is more favourable, CMC decreases. Hence, a smaller number of surfactant molecules are required to form micelles; more oil will be emulsified for the same amount of surfactants. The effects on emulsifying ability differ in the order:  $Ba^{2+}>K^+>Na^+$ . This is supported by the data as shown in Graph 6.1.1 and 6.1.2.

<sup>&</sup>lt;sup>68</sup> Arunima Chaudhuri, Sourav Haldar, Amitabha Chattopadhyay. Organization and dynamics in micellar structural transition monitored by pyrene fluorescence. *Biochemical and Biophysical Research Communications* [Online] **2009**, *390(3)*, 728-732 http://dx.doi.org/10.1016/j.bhrc.2009.10.037 (Accessed June 2, 2013)

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### 9.2 Appendix B: Standardization of HNO<sub>3</sub> & Concentration of Cations

#### Concentration Na<sub>2</sub>CO<sub>3</sub>

**ETHER SULPHATE?**"



Initial mass of reagent bottle/g ±0.001g	2.5771
Final mass of beaker and NaNO <sub>3</sub> /g ±0.001g	2.7473
Mass of NaNO₃ used/g ±0.002g	0.1702

#### Table 9.2.1: Mass of NaNO3

#### Concentration NaNO3

ETHER SULPHATE?"



Concentration of NaNO<sub>3</sub> utilized is (0.100±0.001)moldm<sup>-3</sup>

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Soap - Ba(NO3)2 solution

Calculations	Propagation of uncertainties
Volume of HNO <sub>3</sub> used = $\frac{14.60+14.60}{2}$	$\pm$ % $\Delta$ Vol. Of HNO <sub>3</sub> used = $\pm \left(\frac{0.10+0.10}{2}\right)$
= 14.60 cm <sup>3</sup>	$= \pm 0.10$ cm <sup>3</sup>
Amount of HNO <sub>3</sub> used = $\frac{14.60}{1000}$ x 2.005 $\approx 0.02928$ mol	$\pm$ %Δ Amount of excess NaOH = $\pm$ %Δamount of HNO <sub>3</sub> used
n(excess NaOH) = 0.02928mol	±%Δ(excess NaOH) = $\frac{0.10}{14.60}$ × 100% + 0.919% ≈ ±1.604%
Amount of NaOH reacted = 0.0600 – 0.02928 = 0.03073mol	±Δ amount of NaOH reacted= ±(0.0003+1.604% x 0.02928) ≈ ± 0.0007696
Amount un-emulsified oil = 0.03073 ÷ 3 ≈ 0.01024mol	±4 amon of un-emulsified oil = ±0.0007969 ÷ 3 ≈ ±0.0002565mol
Amount emulsifiend = $0.01525 - 8$ 0.01024 = 0.01525 - 8 $\approx 0.0699 = 8$	$\pm \Delta$ amount of emulsified oil = ±(0.00022+0.0002565) ≈ ±0.00048mol

Amount of emulsified oil is (0.00501±0.00048)mol

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Detergent - Ba(NO<sub>3</sub>)<sub>2</sub> solution

Calculations Volume of HNO <sub>3</sub> used =	$\frac{15.00+15.00}{2}$ = 15.00cm <sup>3</sup>	Propagation of uncertainties ±%Δ Vol. Of HNO <sub>3</sub> used = $\pm \left(\frac{0.10+0.10}{2}\right)$ = $\pm 0.10$ cm <sup>3</sup>
Amount of HNO <sub>3</sub> used =	15.00/1000 x 2.005 ≈ 0.03008mol	$\pm$ % $\Delta$ Amount of excess NaOH = $\pm$ % $\Delta$ amount of HNO <sub>3</sub> used
n(excess NaOH) = 0.030	)08mol	±%Δ(excess NaOH) = $\frac{0.10}{15.00}$ × 100% + 0.919% ≈ ±1.586%
Amount of NaOH reacte 0.03008	d = 0.0600 – = 0.02993mol	±∆ amount of NaOH reacted= ±(0.0003+1.586% x 0.02346) ≈ ± 0.0007769mol
Amount un-emulsified oi	I = 0.02993 ÷ 3 ≈ 0.009975mol	$\pm 4$ and $100$ un-emulsified oil = $\pm 0.0007769 \div 3$ $\approx \pm 0.0002590$ mol
Amount emulsifier th= 0.09997	0.01525 - 9 0.06329 - 9	$\pm \Delta$ amount of emulsified oil = ±(0.00022+0.0002590) ≈ ±0.00048mol

Amount of emulsified oil is (0.00528±0.00048)mol